



## **A method for manufacturing a tool part for an injection molding process, a hot embossing process, a nano-imprint process, or an extrusion process**

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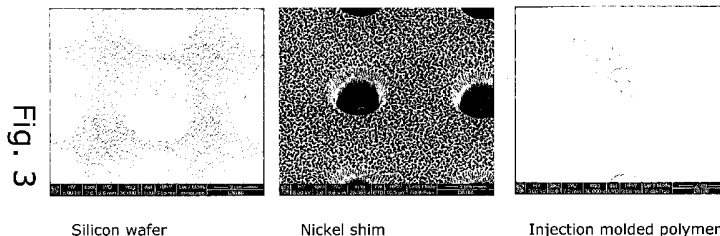
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(54) Title: A METHOD FOR MANUFACTURING A TOOL PART FOR AN INJECTION MOLDING PROCESS, A HOT EM-BOSSING PROCESS, A NANO-IMPRINT PROCESS, OR AN EXTRUSION PROCESS



(57) Abstract: The present invention relates to a method for manufacturing a tool part for an injection molding process, a hot embossing process, nano-imprint process or an extrusion process. First, there is provided a master structure (10) with a surface area comprising nanometre-sized protrusions (11) with a minimum density of approximately 105 protrusions/mm<sup>2</sup>, the protrusions being positioned in a non-periodic, irregular pattern, said protrusions being created by a process comprising alternating passivation and etching into the master structure. Secondly, there is made a transfer of the master structure into a metal insert (20), the metal insert having a corresponding nanometre-sized pattern (21) from said protrusions, and thirdly, adapting the metal insert into a tool part (30) for enabling nanometre-sized patterns being formed by the tool part. The invention provides an easier and faster way of manufacturing the master structure, e.g. a black silicon wafer. It is a further advantage of the present invention that it provides an advantageous way of making tools capable of producing self-cleaning surfaces without the need for chemical coating.



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A METHOD FOR MANUFACTURING A TOOL PART FOR AN INJECTION MOLDING PROCESS, A HOT EMBOSSING PROCESS, A NANO-IMPRINT PROCESS, OR AN EXTRUSION PROCESS

## 5 FIELD OF THE INVENTION

The present invention relates to a method for manufacturing a tool part for an injection molding process, a hot embossing process, a nano-imprint process, or an extrusion process. The invention also relates to corresponding tool part, e.g. a tool part capable of producing a self-cleaning surface in an object.

10

## BACKGROUND OF THE INVENTION

Injection molded polymer parts with micro- or nano-structured surfaces, has the ability to introduce wide range of new functionalities. Many consumer products  
15 today, use chemical coatings to lower adhesion or to repel water, these are potentially unhealthy or toxic. Surfaces with self-cleaning nano and microstructures that imitate the lotus flower. This is of high relevance for the medical and food producing industries. For example, medical and food containers can be designed so they can be completely emptied. Therefore, none of the  
20 expensive medicine or food is wasted. Furthermore, self-cleaning surfaces are relevant for hearing aids and medical equipment such as endoscopes.

Various solutions have been suggested in the past in order to meet this demand for self-cleaning surfaces. Solutions are available but they are either rather  
25 complicated to manufacture due to the intensive need for lithographic processing , or they are not sufficiently durable over time, e.g. by being dependent on chemical coatings that are worn off during use. Some chemical coatings used in consumer products today use e.g. fluorine containing chemical coatings, which are potentially unhealthy or toxic.

30

US patent application 2002/0164443 for example discloses an injection molding processes with the purpose of creating lotus-like structures with various mathematically based structures. Initially, a master structure is made which is then transferred into an injection-molding tool, for example by a LIGA process.  
35 The production of the master structure is however quite time consuming due to

the intensive need for complex, and therefore costly, lithography steps for designing the proposed mathematical structures resulting in a lotus-like functionality in the final product.

- 5 US patent application 2007/115554 relates to an antireflective viewing surface with a textured layer disposed upon the viewing surface; wherein the textured layer comprises randomly distributed protrusions having randomly distributed dimensions that are smaller than the wavelength of light. Disclosed herein is a method of manufacturing an antireflective viewing surface comprising:
- 10 electroforming a metal upon a first template to form an electroformed metal template; wherein the first template comprises random, columnar structures; disposing a layer of a polymeric resin on a viewing surface; pressing the electroformed metal template against the viewing surface; and solidifying the polymeric resin. The layer having randomly distributed protrusions of e.g. titanium
- 15 dioxide or carbon nanotube is grown on the surface by conventional methods. The protrusions have dimensions smaller than the wavelength of light in order to provide anti-reflection. The textured layer can be transferred from a so-called first template to an electroformed metal template that can be used for subsequent molding, or forming, cf. figure 4 and the corresponding description [0058]. The
- 20 growth of such protrusions is typically somewhat time-consuming thereby representing a bottle neck for manufacturing use.

Hence, an improved method would be advantageous, and in particular a more efficient and/or reliable method would be advantageous.

25

## OBJECT OF THE INVENTION

It is a further object of the present invention to provide an alternative to the prior art.

30

In particular, it may be seen as an object of the present invention to provide a method that solves the above mentioned problems of the prior art with complex and/or cost intensive manufacturing of tools part having functional surfaces.

35

## SUMMARY OF THE INVENTION

Thus, the above described object and several other objects are intended to be obtained in a first aspect of the invention by providing a method for

5 manufacturing a tool part for an injection molding process, a hot embossing process, nano-imprint process or an extrusion process, the method comprises

providing a master structure with a surface area comprising nanometre-sized protrusions with a minimum density of approximately  $10^5$  protrusions/mm<sup>2</sup>, the  
10 protrusions being positioned in a non-periodic, irregular pattern, said protrusions being created by a process comprising:

alternating passivation and etching into the master structure,

and/or

simultaneous passivation and etching into the master structure,

15 and/or

etching into the master structure,

transferring the master structure into a metal insert, the metal insert having a corresponding nanometre-sized pattern from said protrusions, and

20 adapting the metal insert into a tool part for enabling nanometre-sized patterns being formed by the tool part.

The invention is particularly, but not exclusively, advantageous for obtaining a tool part in a more simple way than hitherto possible due the easier and/or faster  
25 way of manufacturing the master structure, e.g. in a semiconductor material such as a silicon wafer. It is a further advantage of the present invention that it provides an advantageous way of making tools capable of producing self-cleaning surfaces without the need for chemical coating.

30 Furthermore, an injection molding tool part according to the present invention can essentially manufacture final products in any thermoplastic material suitable for injection molding which may open up for wide spread application of the present invention, e.g. in every day consumer products already manufactured by injection molding.

35

In the context of the present invention, it is to be understood that the three options, (1, 2 and 3) for creation of protrusions:

- 1) alternating passivation and etching into the master structure,  
and/or
  - 5 2) simultaneous passivation and etching into the master structure,  
and/or
  - 3) etching into the master structure,
- can be applied solely (i.e. only option 1, 2 or 3), in combination (i.e. 1 and 2, or 1 and 3, or 1 and 3), such as a period of performing option 1 followed by another
- 10 period with option 2, etc., and a combination of all 3 options (1, 2, and 3), such as various combination of periods with options 1, 2, and 3 for creation of protrusions, as the skilled person will readily understand once the general principle of the invention is comprehended.
- 15 Notice that the present invention applies various etching processes, which is quite different from US patent application 2007/115554 where the random protrusions are grown, typically over several hours. The present invention is typically order of magnitude faster and less complex to implement, in particular when implemented on a semiconductor wafer or similar in a cleanroom environment. In general, the
- 20 present invention relates to a master structure made of a non-metal, such as a semiconductor material.

The present invention is further advantageous over US2007/115554 in that the master origination is compatible with standard processes available in most

25 cleanrooms for semiconductor fabrication, the term 'origination' meaning the way of modifying the master structure (in short the 'master') into a desired shape. Moreover, the present invention does not include nanoparticle coatings with potential health hazards, as the master structure is formed by structuring the substrate surface exclusively, or predominately, by etching processes in the most

30 preferred embodiments. Finally, the present invention is primarily focussed on anti-wetting functionalities, though the present invention may also be applied in order to implement anti-reflection properties in the final product being manufactured by the tool according to the first aspect of the invention.

The present invention relates generally to tool parts for application in an injection molding process, a hot embossing process or an extrusion process, or other similar processes or equivalent manufacturing processes.

- 5 The master structure may have alternatively have a surface area comprising nanometre-sized protrusions with a minimum density of approximately  $10^4$  protrusions/mm<sup>2</sup>, or alternatively approximately  $10^6$  protrusions/mm<sup>2</sup>. It is to be understood that the density is calculated on an average basis as will be appreciated by a person working with micro-technologies.

10

- The concept of a non-period, irregular pattern is to be understood by the skilled person as seen on as seen or viewed on a nanometer scale, e.g. using scanning electron microscopy (SEM) or an atomic force microscopy (AFM) as it will be demonstrated in the detailed description of the invention below. Using for  
15 example a pixel size of approximately 2-20 nm in SEM, the master structure will be shown to have a protrusion distribution with such a pattern.

- The process for creating said nano-meter sized protrusions using alternating, and/or simultaneous, passivation and etching into the master structure may  
20 preferably take place in a vacuum chamber, more preferably the entire process of creating the protrusions takes place in a single vacuum chamber in order to facilitate fast processing i.e. without any significant delay between etching and passivation. Thus, by performing the process in a single process the invention may facilitate that the master structure is made in a quick way, e.g. less than 60  
25 minutes, less than 30 minutes, or less than 10 minutes. Typically, the alternating process of passivation and etching into the master structure may be repeated a plurality of times, such as least 10 times, 50 times, 100 times, or 500 times.

- Similarly, if the process for creating said nano-meter sized protrusions in a non-  
30 period, irregular pattern is obtained using etching into the master structure, e.g. by a chemical wet etching process in strong acid or base, the process may also be take place in a fast and advantageous way.

- The step of transferring the master structure into a metal insert, the metal insert  
35 having a corresponding nanometre-sized pattern from said protrusions can be

made either by a positive transfer, or by a negative transfer of the master structure as the skilled person would readily understood once the general teaching and principle of the present inventions has been appreciated by the skilled person. There may be several intermediate steps in the transferring process. There may  
5 also be produced several duplicates ('families') of the same master structure.

The step of adapting the metal insert into a tool part can be performing in various ways, e.g. by mechanical securing the metal insert into the tool part. The adaption must be made so as to enable that the nanometre-sized patterns of the  
10 insert is replicated or formed into the moulded product by the tool part.

Preferably, the process for creating the protrusions may result in a random shape and/or a random position with respect to an individual protrusion i.e. essentially the process may be viewed as a non-deterministic process, though of course some  
15 overall control of the average shape and position of the protrusions are possible. Nevertheless, the advantage in speed of manufacturing outweighs this apparent disadvantage. More specifically, the dimensions of the protrusions may defined by corresponding intervals for each dimension, each dimension being randomly scattered within a corresponding interval, preferably at least one dimension  
20 having a scattering of at least 50% of the average value e.g. height of the protrusion may be a height range of : average height +/- 100%, 80%, 60%, 40%, 20% etc. or a thickness, or width, with a thickness range of : average thickness +/- 100 %, 80%, 60%, 40%, 20% etc.

25 Alternatively, the process may be defined by a set of global process parameters, said parameters being common for the creation of at least a main portion of the protrusions such as gas, bias, temperature, pressure, switching frequency etch/passivation. Thus, there are no process parameters related to the individual protrusions like for instance in conventional lithography. Thus, the process may be  
30 defined by a set of process parameters, said parameters not being directly related to the size and/or the position of the individual protrusion.

It may be said that the nanometer-sized protrusions may be created by the process does not require any lithographic process step for defining shape and/or



position of the protrusions, at least for the main part of the protrusions. The main part of the protrusions may e.g. 90% or 95%.

Typically, the passivation may comprise the formation of an inert polymer, or an oxide, on the master structure, using e.g. a fluoro-carbon like C<sub>3</sub>F<sub>4</sub> for creating such a temporarily layer. Preferably, the etching may comprise reactive ion etching (RIE) in the master structure e.g. Bosch or cryogenic.

Alternatively or additionally, the etching may comprise a wet chemical etching such as a strong base, or acid, e.g. KOH. The master structure, e.g. a silicon wafer, is submerged in the etching liquid which makes the surface rough or etches in certain crystallographic plane. A mask may be used or not. A possible mask is a photoresist or SiO<sub>2</sub>/Nitride.

Alternatively, wherein the etching may comprise laser-assisted etching, such as femtosecond pulse laser process as described by Crouch et al. in Appl. Phys. Lett. 84, 1850 (2004); doi: 10.1063/1.1667004, which is hereby incorporated by reference in its entirety.

Typically, the master structure is a semiconductor wafer, a glass wafer, a metal wafer, or a ceramic wafer, as it will be appreciated by the skilled person. Thus, in one embodiment, the master structure may be a silicon wafer, and preferably the nanometer-sized protrusions constitute nano-grass and/or black silicon. Black silicon is a known surface type produced by e.g. repeated directional etching and passivation resulting in large amount of needle-like, or spike-like, structures pointing away from the surface, the surface has a relatively low reflectivity (hence the name). Nano-grass may similarly be defined as a large amount of protruding, randomly oriented structures resembling to some extent natural grass as seen in a microscopic view.

30

Typically, the nanometer-sized protrusions may have an aspect ratio (A), i.e. height / width of structure on average, of minimum 10, 1, 0.1 or 0.01.

Alternatively, the nanometer-sized protrusions may have an aspect ratio (A), i.e. height / width of structure on average, of maximum 10, 1, 0.1 or 0.01.

35

Typically, the nanometer-sized protrusions have a density within an interval of  $10^3$  -  $10^{10}$  /mm<sup>2</sup>, preferably within an interval of  $10^4$  -  $10^7$  /mm<sup>2</sup>.

Advantageously, the nanometer-sized protrusions may have an average height of  
5 minimum 10 nm, 20 nm, 30 nm, 40 nm, 50 nm or 100 nm, 200 nm, or 300 nm.  
Alternatively, the nanometer-sized protrusions may have an average height of  
maximum 10 nm, 20 nm, 30 nm, 40 nm, 50 nm or 100 nm, 200 nm, or 300 nm.

The dimensions of the protrusions should, on one hand satisfy the functional  
10 purpose of e.g. providing a self-cleaning surface by having sufficiently high  
protrusions, and, on one the other hand, being within a feasible level of  
manufacturing and durability. Thus, too high protrusions may be difficult to mold,  
e.g. un-molding, and may wear off quickly during mechanical stresses during  
applications.

15

In one preferred embodiment, the master structure may comprise a hierarchical  
structure with a plurality of surface areas comprising nanometre-sized protrusions  
with a minimum density of  $10^5$  protrusions/mm<sup>2</sup>, and a plurality of surface areas  
20 comprising micrometer-sized surface structures, either protruding away from the  
surface and/or being holes in the surface, the said structures preferably having a  
characteristic length scale of 1-1000 micrometer, more preferably 1-100  
micrometre, even more preferably 2-50 micrometer. Such a hierarchical structure  
is particularly advantageous for obtaining self-cleaning functional properties of the  
25 resulting surface. The nanometre-sized protrusions may cover, i.e. being  
positioned upon, both the micrometer-sized surface structures protruding away  
from the surface and/or the holes in the surface, and possibly the surface not  
being protruded or lowered relative to the overall or average surface level.

30 Beneficially, the step of transferring the master structure into a metal insert may  
be performed by method chosen from the list consisting of:

- material deposition, such as electroplating
- imprint lithography,
- soft lithography,

- hot embossing combined with etching, and
- casting.

Other available transferring techniques may readily be considered by the skilled  
5 person once the general teaching and principle of the present invention is  
acknowledged. Thus, both inverse transfer (negative) and direct transfer  
(positive) of the master is envisioned within the context of the present invention.

Particularly, the transferring the master structure into a metal insert may be  
10 performed by electrochemical deposition of a shim on the master structure, the  
shim being used on, or in, the metal insert as a part of the tool part. Beneficially,  
the manufacturing may include duplication of the master into a so-called 'family'  
of shims for facilitating high speed productions.

15 In a second aspect, the invention relates to a tool part having a metal insert with  
nano-meter-sized protrusions, the protrusions being manufactured according to  
the first aspect.

In a third aspect, the present invention relates to a polymer product manufactured  
20 by a tool according to the second aspect.

Such as product is particularly beneficial in that the fabrication of a hierarchical  
surface structure may comprise both micro and nanostructures, where the  
microstructure is e.g. composed of holes rendering the surface repellent such that  
25 liquid is prevented from wetting the surface inside the holes due to surface  
tension when the entire surface is covered by liquid. This will of course depend on  
the properties of the master structure as will readily be understood.

Alternatively or additionally, the combination of micro- and nanostructures may  
30 ensure that the structured surface is self-cleaning, e.g. such that sessile drops will  
form high contact angles with the surface, as measured with water (WCA), and in  
addition the contact angle hysteresis between advancing and receding contact  
angle is small. A high contact angle may be considered to be above  $130^\circ$  and  
more preferably above  $150^\circ$ , while a low contact angle hysteresis may be  
35 considered to be below  $30^\circ$ , and more preferably below  $5^\circ$ . An advantageous use

of such a surface will be the inside of liquid containers, e.g. paint, dairy products, or cosmetics, and will ensure that the liquid container can be emptied and/or cleaned more easily.

- 5 The individual aspects of the present invention may each be combined with any of the other aspects. These and other aspects of the invention will be apparent from the following description with reference to the described embodiments.

#### BRIEF DESCRIPTION OF THE FIGURES

10

The invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

15

Figure 1 shows a schematic overview of the three main steps of the invention; providing a master structure, transferring to a metal insert, and adapting to a tool part,

- 20 Figure 2 shows schematically a more detailed illustration of a method according to the present invention,

Figure 3 shows three SEM images of a master structure in silicon, a Nickel shim where the hierarchical structure with nanometre-sized and micrometre-size

- 25 pattern has transferred to, and a resulting molded polymer product,

Figures 4 and 5 shows more detailed SEM images of a silicon master structure according to the present invention,

- 30 Figure 6 shows a more detailed AFM image of silicon master structure,

Figure 7 shows SEM images of a Nickel metal insert according to the present invention,

Figure 8 shows a more detailed AFM image of a Nickel metal insert according to the present invention,

Figures 9 and 10 shows SEM images of a molded polymer product manufactured with tool according to the present invention,

5

Figure 11 illustrates the result of the wetting experiment for a flat structure without the invention (left) and a polymer product manufactured with tool according to the present invention (right), and

10 Figure 12 is a schematic system-chart representing a method according to the invention.

#### DETAILED DESCRIPTION OF AN EMBODIMENT

15 Figure 1 shows a schematic overview of the three main steps forming part of the invention; providing a master structure 10, transferring to a metal insert 20, and adapting to a tool part 30.

The master structure 10 has a surface area comprising nanometre-sized protrusions 11 (not to scale) with a minimum density of approximately  $10^5$  protrusions/mm<sup>2</sup>, the protrusions being positioned in a non-periodic, irregular pattern i.e. essentially a random or non-deterministic pattern, said protrusions being created by a process comprising:

- 25 1) alternating passivation and etching into the master structure, e.g. reactive ion etching by the so-called Bosch method, and/or
- 2) simultaneous passivation and etching into the master structure, e.g. reactive ion etching by the so-called cryogenic method, and/or
- 30 3) etching into the master structure, e.g. by a chemical wet etching.

Subsequently, the pattern of the protrusions 11 is transferred from the master structure 10 into a metal insert 20, the metal insert having a corresponding nanometre-sized pattern 21 from said protrusions, such as a LIGA technique or  
35 other similar or equivalent techniques.

Finally, the step of adapting the metal insert 20 into a tool part 30 is performed for enabling nanometre-sized patterns being formed by the tool part 30. In Figure 1, the tool part is shown to have two half-parts 30a and 30b, respectively, where the metal insert 20 is positioned in the lower part 30b. However, the present  
5 invention is contemplated also to include a plurality of metal inserts like the one shown in Figure 1. Also schematically indicated are feeding channel 31 for supplying molten polymer under pressure into the molding chamber 32 of the tool 30.

10 Figure 2 shows schematically a more detailed illustration of a method according to the present invention. The fabrication for the insert 30 with combined nano structures is described step by step as indicated by number 1-9 right of the panel; the size range is 1µm (micrometer) to 100 µm for the micro structures and 50 nm to 2500 nm for the nanostructures (black silicon)

15

The method has the following steps:

1. The starting point of the insert fabrication is a new wafer of silicon.
- 20 2. A resist layer is deposited on the wafer; this could be done by spin coating, spray coating as well as other methods.
3. The microstructures is defined in the resist with lithography e.g. UV, E-beam, Imprint etc. The resist is then developed leaving the structures in the resist layer.
- 25 4. The microstructures are transferred to the wafer e.g. by reactive ion etching.
5. The resist layer is stripped leaving the microstructures in the wafer.
- 30 6. Black silicon is etched, to produce nano structures having protrusions 11 in the master structure. One of several methods for producing so-called black silicon surfaces is to apply the so-called Bosch process for reactive ion etching (RIE), where a black silicon structure can be achieved by repeatedly switching between etching and passivation.

35

7. Three options can for example be used to transfer the structures from the wafer to the insert. 1) material depositing such as electroplating 2) imprint lithography, soft lithography, or hot embossing followed by etching by either reactive ion etching, or sputtering, or 3) Casting. As indicated by the  
5 corresponding pattern or protrusions 21, as visible and separated in step 8, the protrusions 11 are accordingly transferred from the master 10 into the insert 20.

8. An insert made of softer materials such as aluminium or nickel, cannot withstand as many injection molding cycles as tool steel. The insert therefore may  
10 optionally require a hard coating to make it more durable or a coating to make demolding easier.

9. The final step is repeating injection molding or embossing cycles, for the mass production of super hydrophobic/super hydrophilic and self-cleaning polymer parts  
15 35.

Figure 3 shows three SEM images of a master structure in silicon (left), a nickel shim where the hierarchical structure with nanometre-sized and micrometre-size pattern has been transferred to (middle), and a resulting molded polymer product  
20 (right). Notice how the etched shape of the protrusions and the overall hierarchical structure is transferred from the master structure 'negatively' to the nickel shim, and the resulting polymer product therefore being a 'positive' transfer of the silicon master structure.

25 An injection molding insert with microstructures (circular pillars) in the size range 3 to 7  $\mu\text{m}$  with a pitch 3 to 16  $\mu\text{m}$  (on mask) has been fabricated with photolithography and DRIE of a silicon wafer. In addition nanostructures were added by etching so-called black silicon. The process time was 8 min, gas flow SF<sub>6</sub>: 70 sccm and O<sub>2</sub> :110 sccm. Plasma generators settings was 13.56 MHz coil,  
30 2700W 13.56 MHz, platten 30w and platten (substrate) temperature -10 °C. Further details on producing black silicon can be found in a recent review article by Shieh et al. in Phys. D: Appl. Phys. 44 (2011) 174010 *Plasma-made silicon nanograss and related structures*, which is hereby incorporated by reference in its entirety. Without being bound by any specific theory, it is believed that etching  
35 fluorine radicals and passivating oxide radicals are competing, and at a certain

level of oxygen there will be created protrusions due to the inherent micromask made up by impurities in the wafer, dust, etc. and the direction of the etching.

The wafer was electroplated with a 320  $\mu\text{m}$  nickel layer. The wafer was removed  
5 in 30% KOH at 80°C, leaving a nickel insert with inverse structures.

Injection molding of microscope slides were carried out in a variotherm injection mold tool. The polymer used was Topas® 8007 and polypropylene, an optical profilometer was used to measure the structure height to 3.2  $\mu\text{m}$ , and results for  
10 this polymer will also be shown below in Figure 4-11. It should be mentioned that the present inventors has also validated the invention in polypropylene (PP) but results are not shown here.

Figures 4 and 5 shows more detailed SEM images of a silicon master structure  
15 according to the present invention.

In Figure 4A, a tilted (30°) SEM image of a silicon master with 3  $\mu\text{m}$  micro holes and black silicon protrusions is shown. In Figure 4B, a SEM image of a silicon master with 7  $\mu\text{m}$  holes and black silicon protrusions is shown. In Figure 4C,  
20 another tilted (30°) SEM images of black silicon in higher resolution is shown, and in Figure 4D, the same black silicon is seen in a top view.

Figure 5 shows two SEM images with tilted (30°) SEM images of Silicon master with micro pillars i.e. micrometre-sized structures, and black silicon structures i.e.  
25 nanometre sized-structures according to the present invention.

Figure 6 shows a more detailed AFM image of a silicon master structure. The AFM image of black silicon has average height measured to be approximately 70nm.

30 Figure 7 shows SEM images of a Nickel metal insert according to the present invention, with tilted (30°) SEM image of nickel shim with inverse structures, both micro structures and nano structures can be seen to the left. To the right, a corresponding top view.



Figure 8 shows a more detailed AFM image of a Nickel metal insert according to the present invention, the AFM image of nickel shim showing inverse structures, micro structures (2.5  $\mu\text{m}$  hole) and also nano structures from the black silicon can be seen.

5

Figures 9 and 10 shows SEM images of a molded polymer product manufactured with tool according to the present invention.

In Figure 9, a tilted (30°) SEM image of an injection molded polymer with 2.5 $\mu\text{m}$  pillars and nanostructures (black SI) is shown, in large scale on the left and small scale on the right.

Figure 10 shows a tilted (30°) SEM image of an injection molded polymer with 5  $\mu\text{m}$  pillars and nanostructures (black silicon). Notice how all the pillars are slightly distorted to one side. This is believed to be caused by the extraction of the molding process.

Figure 11 illustrates the result of the wetting experiment for a flat structure without the invention (left) and a polymer product manufactured with tool according to the present invention. The contact angle was measured to 95° for the non-structured (flat) surface. The contact angle increased to 150° for the micro- and nanometer structures. The injection molded microscopes slides shown were also fabricated in Topas® 8007-04.

Roll off angles measurements were also used to describe super hydrophobic and self-cleaning surfaces. The contact angles shown alone are not sufficient to describe a self-cleaning surface since the drops can be pinned on the structured surface. The injection molded test areas had roll off angles down to 1°. It is nearly impossible to deposit a drop on the surface of one of these test areas. This clearly indicates that the drops do not wet the structures and they are in the so-called Cassie Baxter state. Further systematic studies of contamination and self-cleaning experiments are planned.

Figure 12 is a schematic system-chart representing an out-line of/in detail the operations of the method for manufacturing a tool part for an injection molding

process, a hot embossing process, nano-imprint process or an extrusion process, the method comprises the steps of

- S1** providing a master structure 10 with a surface area comprising nanometre-sized protrusions 11 with a minimum density of approximately  $10^5$  protrusions/mm<sup>2</sup>, the protrusions being positioned in a non-periodic, irregular pattern, said protrusions being created by a process comprising:
- alternating passivation and etching into the master structure, and/or
  - simultaneous passivation and etching into the master structure, and/or
  - etching into the master structure,
- S2** transferring the master structure into a metal insert 20, the metal insert having a corresponding nanometre-sized pattern 21 from said protrusions, and
- S3** adapting the metal insert into a tool part 30 for enabling nanometre-sized patterns being formed by the tool part.

In short, the invention relates to a method for manufacturing a tool part for an injection molding process, a hot embossing process, nano-imprint process or an extrusion process. First, there is provided a master structure 10 with a surface area comprising nanometre-sized protrusions 11 with a minimum density of approximately  $10^5$  protrusions/mm<sup>2</sup>, the protrusions being positioned in a non-periodic, irregular pattern, said protrusions being created by a process comprising alternating passivation and etching into the master structure. Secondly, there is made a transfer of the master structure into a metal insert 20, the metal insert having a corresponding nanometre-sized pattern 21 from said protrusions, and thirdly, adapting the metal insert into a tool part 30 for enabling nanometre-sized patterns being formed by the tool part. The invention provides an easier and faster way of manufacturing the master structure, e.g. a black silicon wafer. It is a further advantage of the present invention that it provides an advantageous way of making tools capable of producing self-cleaning surfaces without the need for chemical coating.

The invention can be implemented by means of hardware, software, firmware or any combination of these. The invention or some of the features thereof can also be implemented as software running on one or more data processors and/or digital signal processors.

5

The individual elements of an embodiment of the invention may be physically, functionally and logically implemented in any suitable way such as in a single unit, in a plurality of units or as part of separate functional units. The invention may be implemented in a single unit, or be both physically and functionally distributed

10 between different units and processors.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is to be interpreted in  
15 the light of the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope  
20 of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

**CLAIMS**

1. Method for manufacturing a tool part for an injection molding process, a hot embossing process, nano-imprint process or an extrusion process, the method  
5 comprises

providing a master structure (10) with a surface area comprising nanometre-sized protrusions (11) with a minimum density of approximately  $10^5$  protrusions/mm<sup>2</sup>, the protrusions being positioned in a non-periodic, irregular pattern, said  
10 protrusions being created by a process comprising:  
alternating passivation and etching into the master structure,  
and/or  
simultaneous passivation and etching into the master structure,  
and/or  
15 etching into the master structure,

transferring the master structure into a metal insert (20), the metal insert having a corresponding nanometre-sized pattern (21) from said protrusions, and  
20 adapting the metal insert into a tool part (30) for enabling nanometre-sized patterns being formed by the tool part.

2. The method according to claim 1, wherein the process for creating the protrusions result in a random shape and/or a random position with respect to an  
25 individual protrusion.

3. The method according to claim 1, wherein the dimensions of the protrusions are defined by corresponding intervals for each dimension, each dimension being randomly scattered within a corresponding interval, preferably at least one  
30 dimension having a scattering of at least 50% of the average value.

4. The method according to claim 1, wherein the process is defined by a set of global process parameters, said parameters being common for the creation of at least a main portion of the protrusions.

5. The method according to claim 1, wherein the process is defined by a set of process parameters, said parameters not being directly related to the size and/or the position of the individual protrusion.
- 5 6. The method according to claim 1, wherein the nanometer-sized protrusions being created by the process does not require any lithographic process step for defining shape and/or position of the protrusions, at least for the main part of the protrusions.
- 10 7. The method according to claim 1, wherein the passivation comprises the formation of an inert polymer, or an oxide, on the master structure.
8. The method according to claim 1, wherein the etching comprises reactive ion etching (RIE) in the master structure.
- 15 9. The method according to claim 1, wherein the etching comprises a wet chemical etching.
10. The method according to claim 1, wherein the etching comprises laser-
- 20 assisted etching.
11. The method according to claim 1, wherein the master structure is a semiconductor wafer, a glass wafer, a metal wafer, or a ceramic wafer.
- 25 12. The method according to claim 1, wherein the master structure is a silicon wafer, and preferably the nanometer-sized protrusions constitute nano-grass and/or black silicon.
13. The method according to claim 1, wherein the master structure comprises a
- 30 hierarchical structure with a plurality of surface areas comprising nanometre-sized protrusions with a minimum density of  $10^5$  protrusions/mm<sup>2</sup>, and a plurality of surface areas comprising micrometer-sized surface structures, the said structures preferably having a characteristic length scale of 1-1000 micrometer, more preferably 1-100 micrometre, even more preferably 2-50 micrometer.

14. The method according to claim 1, wherein transferring the master structure into a metal insert is performed by method chosen from the list consisting of:

- material deposition, such as electroplating
- imprint lithography,
- 5   • soft lithography,
- hot embossing combined with etching, and
- casting.

15. The method according to claim 1, wherein transferring the master structure  
10 into a metal insert is performed by electrochemical deposition of a shim on the master structure, the shim being used on, or in, the metal insert as a part of the tool part.

16. A tool part (30) having a metal insert (20) with nano-meter-sized protrusions  
15 (21), the protrusions being manufactured according to any of the preceding claims.

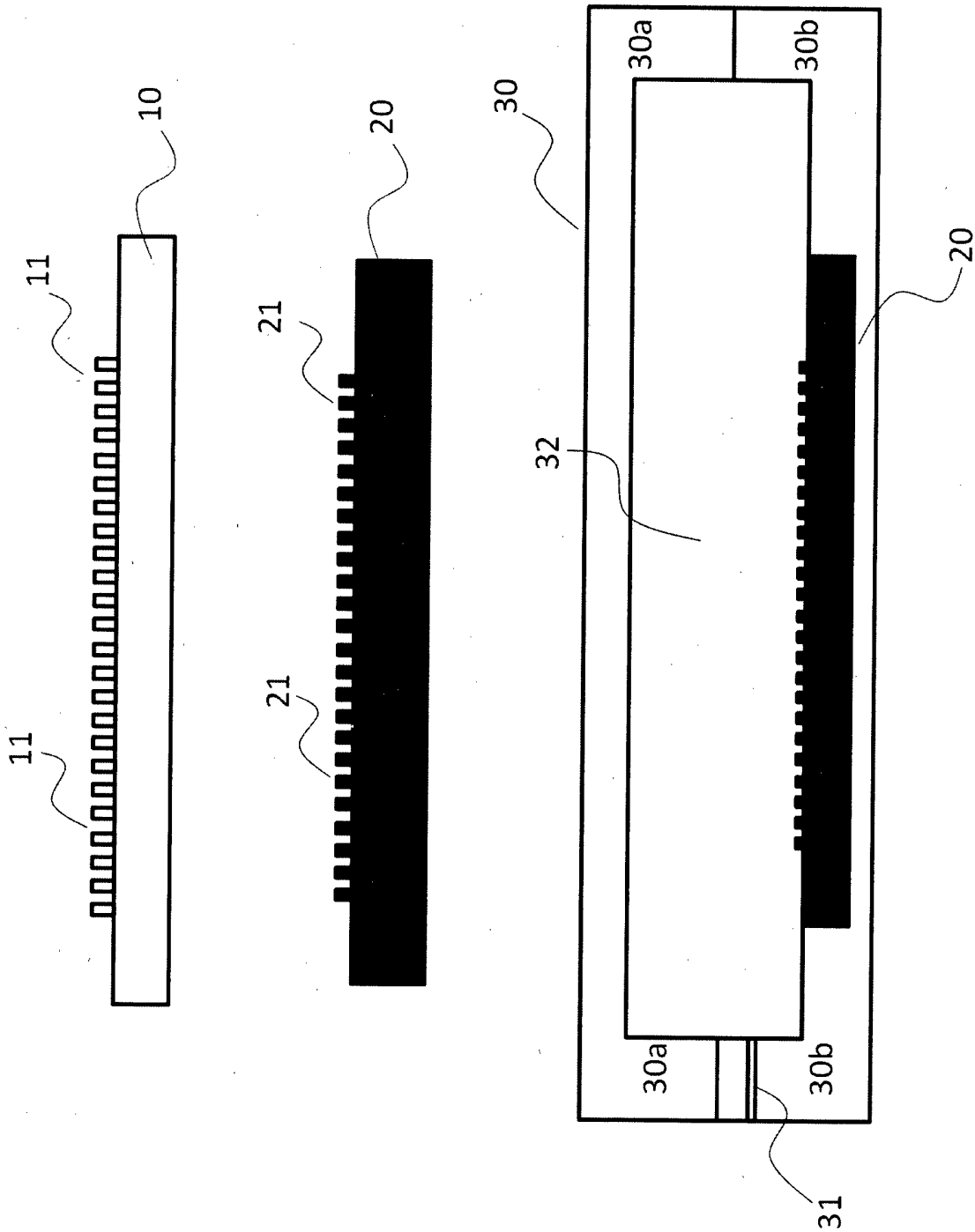


Fig. 1

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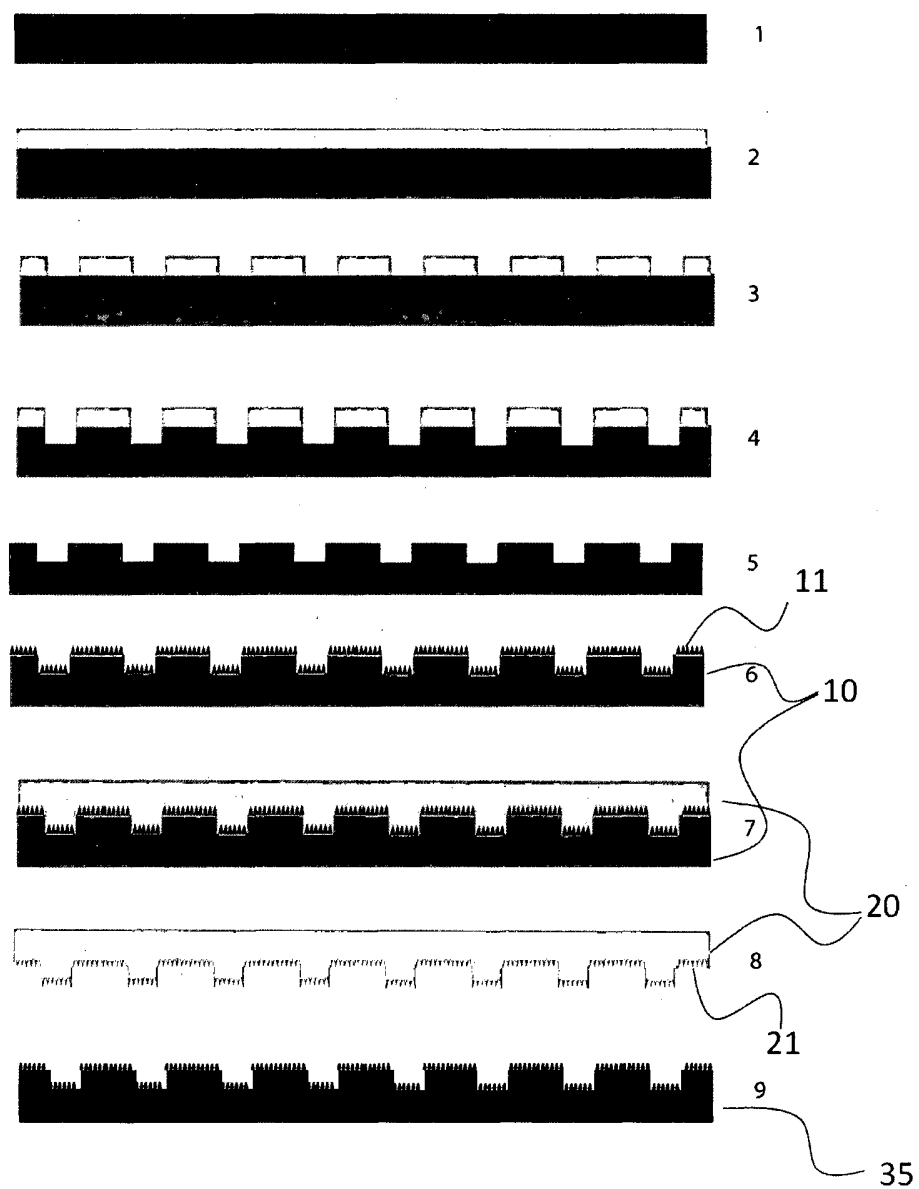
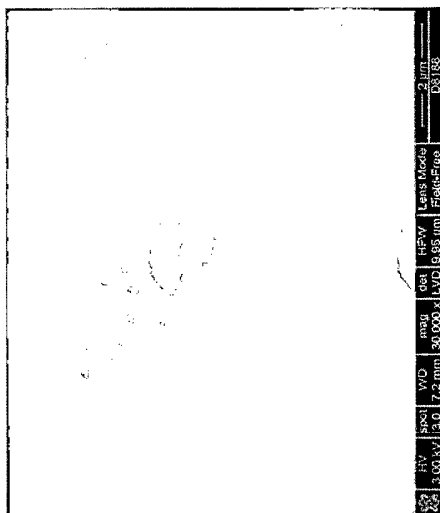


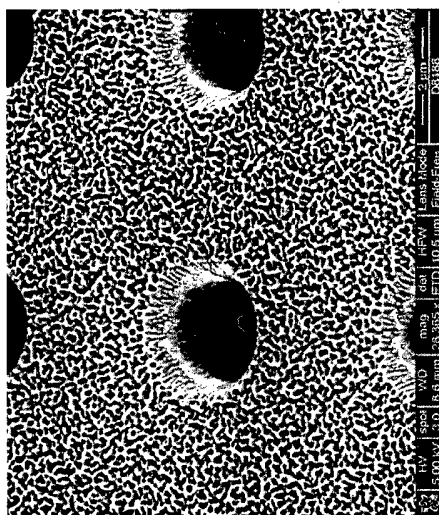
Fig. 2



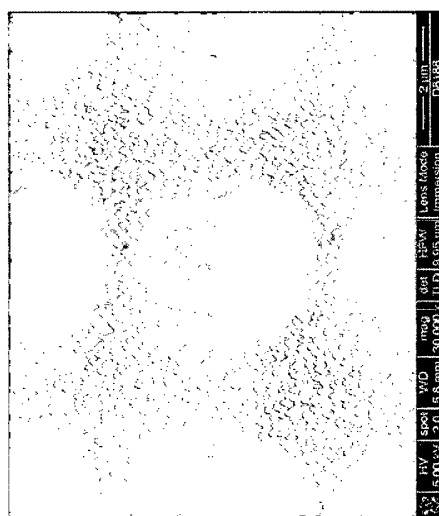
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## Injection molded polymer



## Nickel shim



## Silicon wafer

**Fig. 3**

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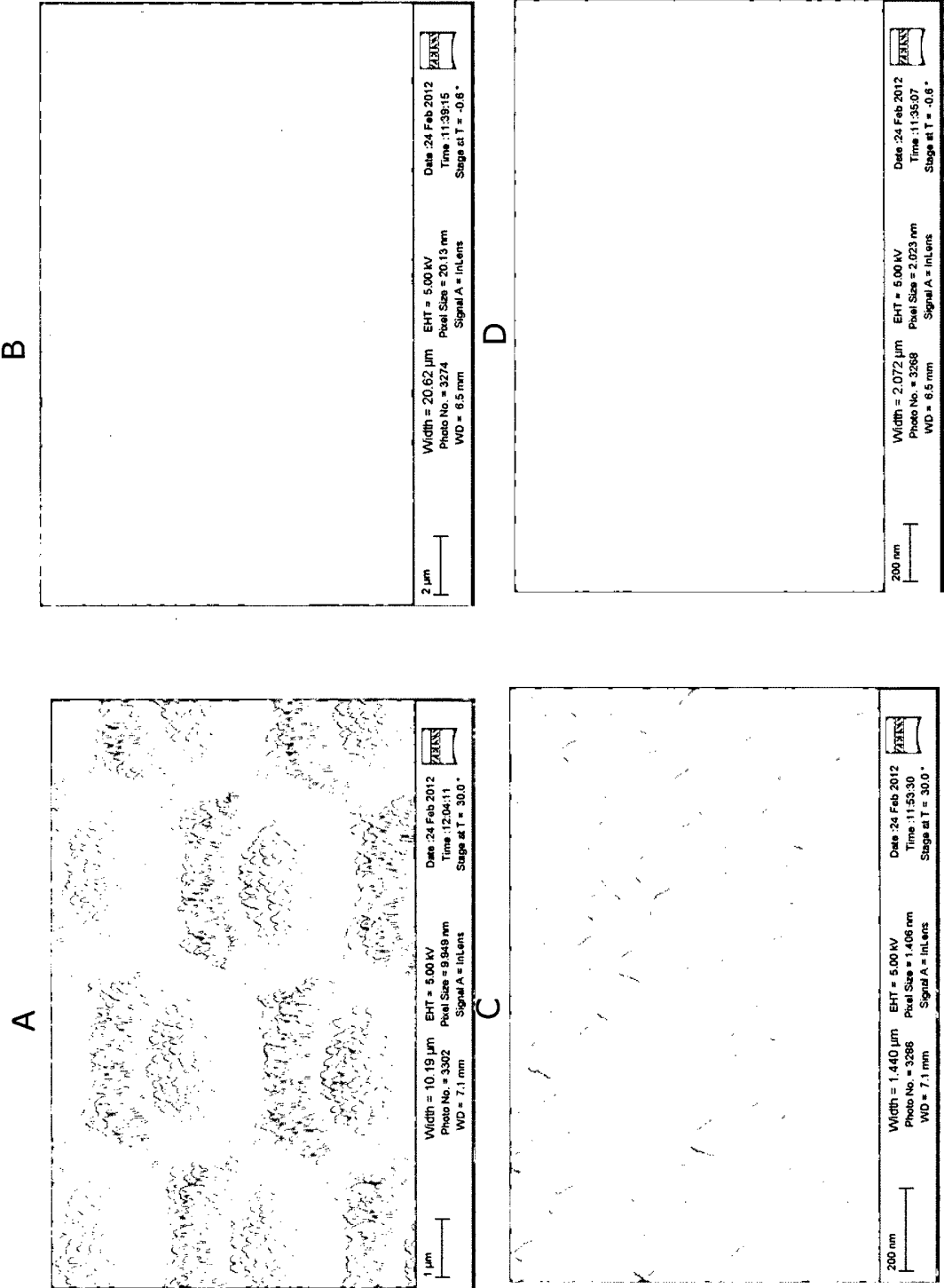


Fig. 4

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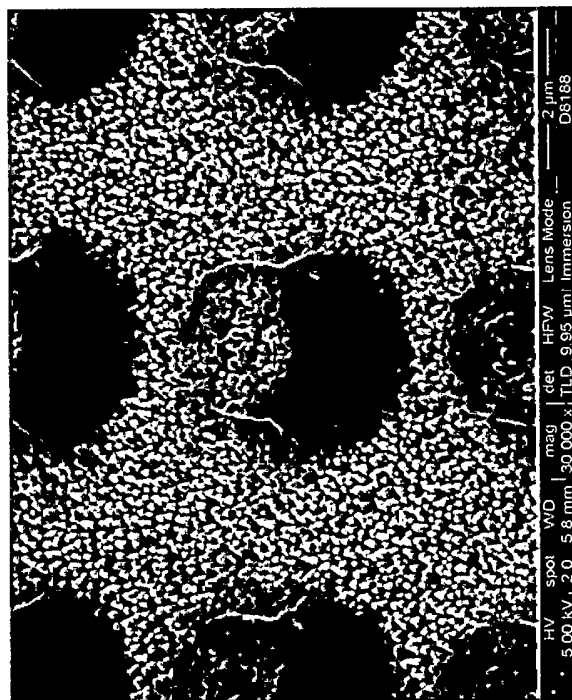
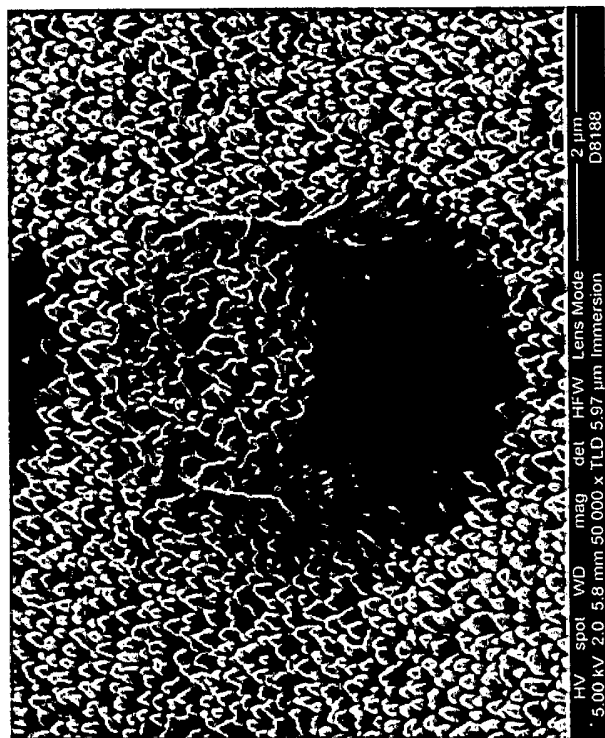


Fig. 5

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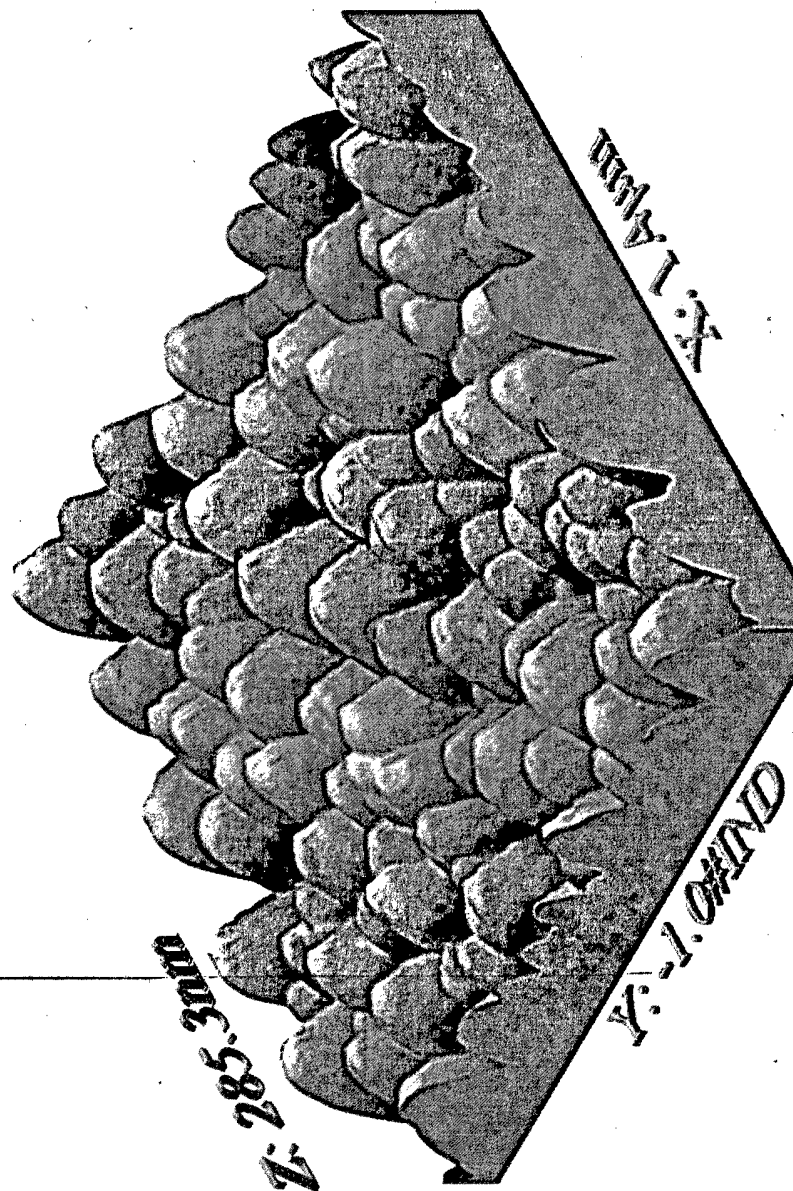


Fig. 6

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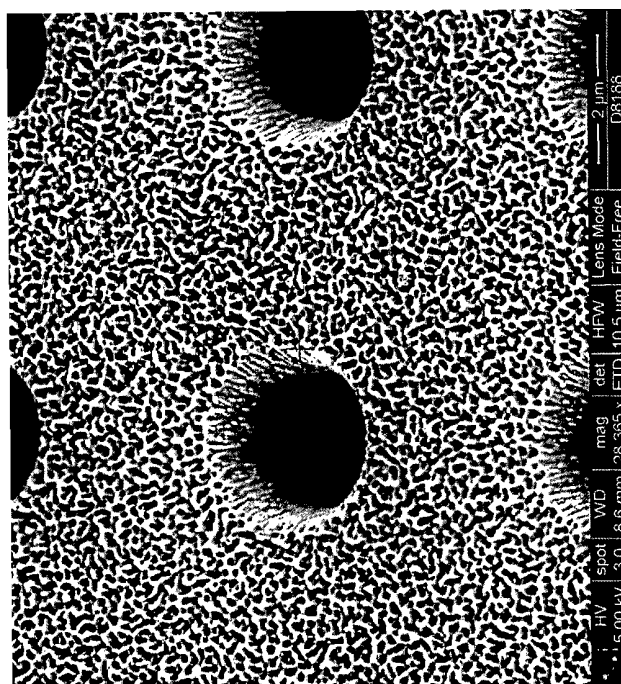
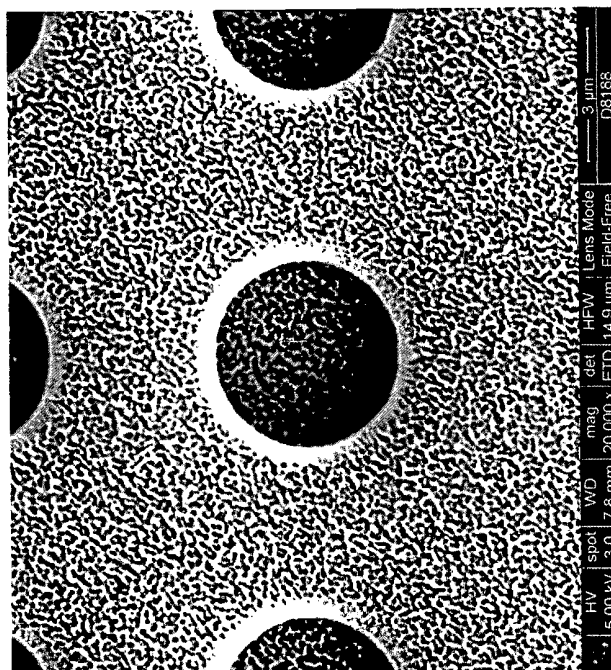


Fig. 7

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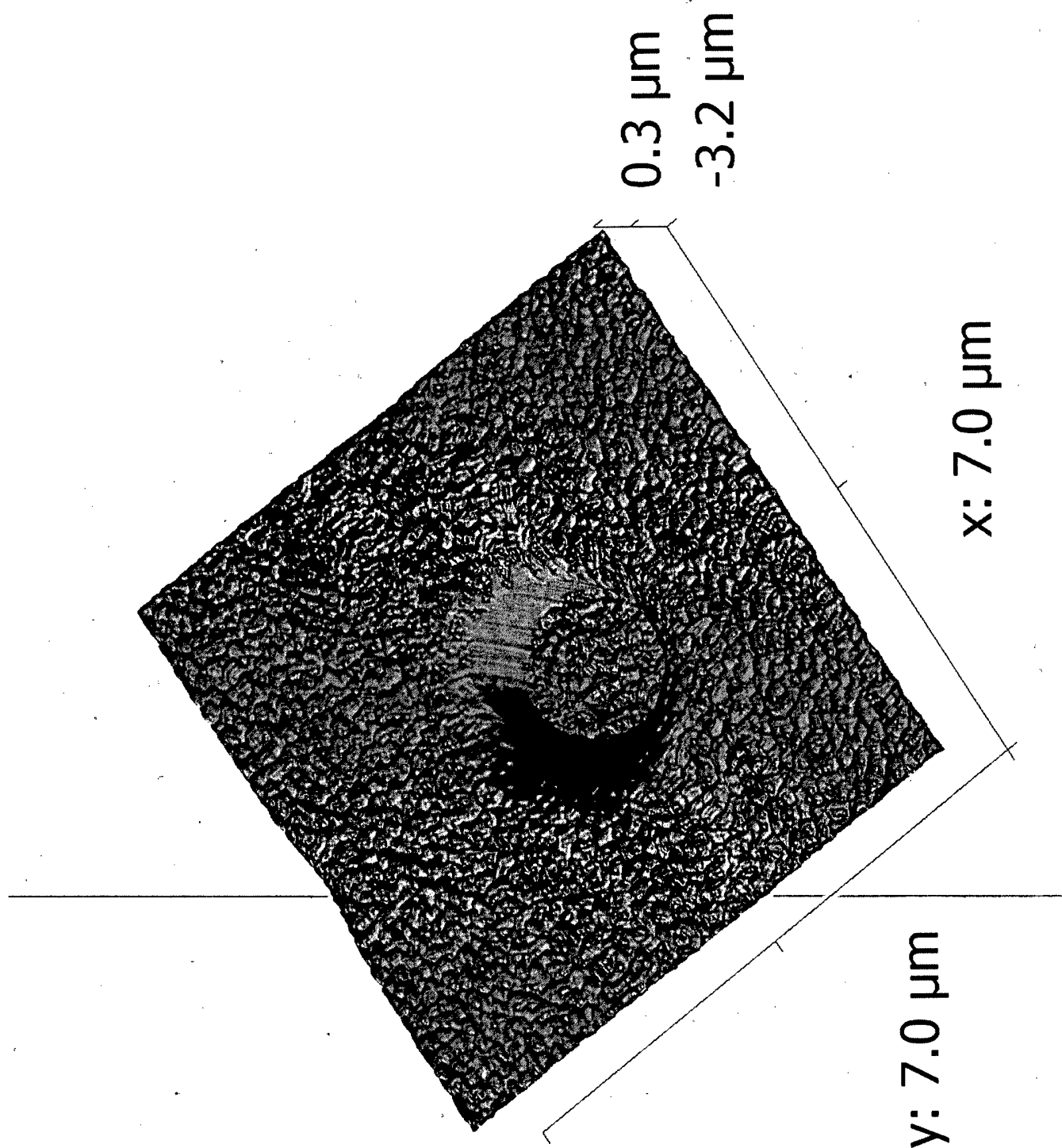


Fig. 8

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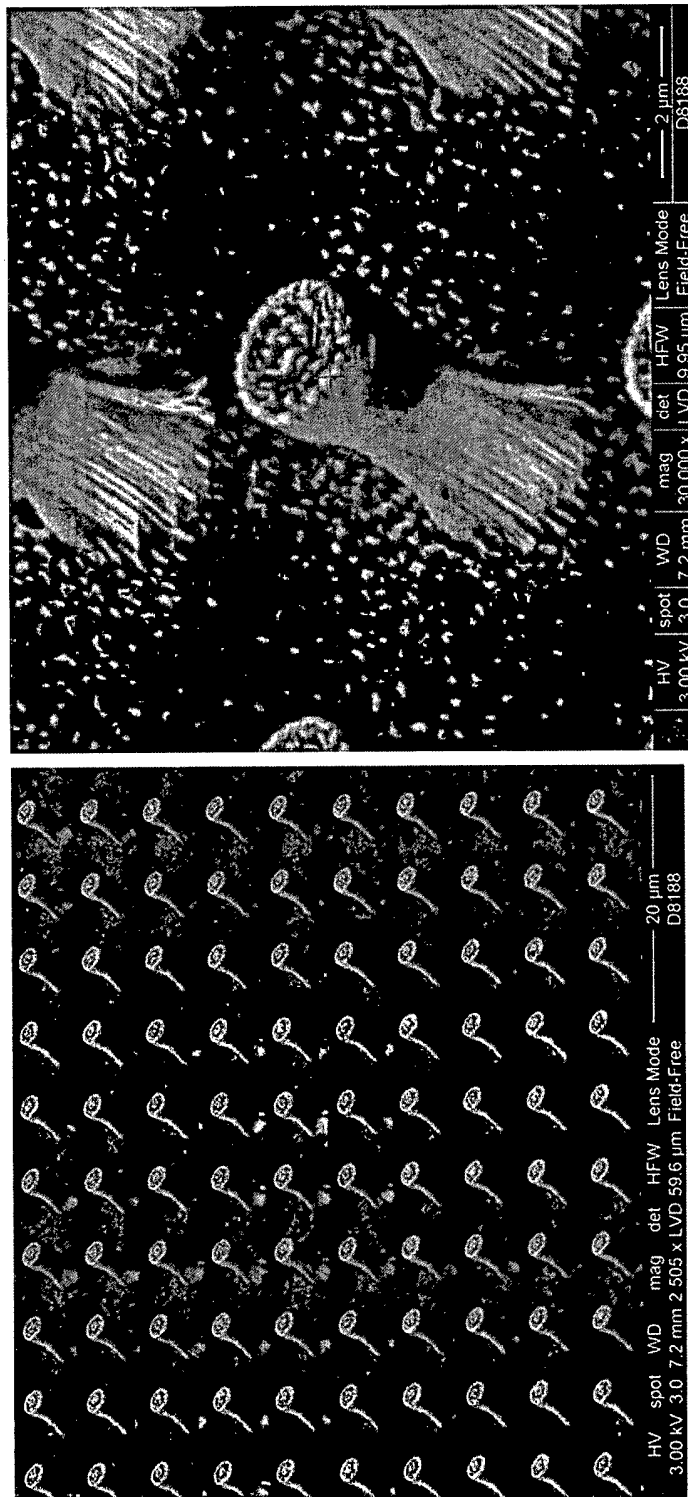


Fig. 9

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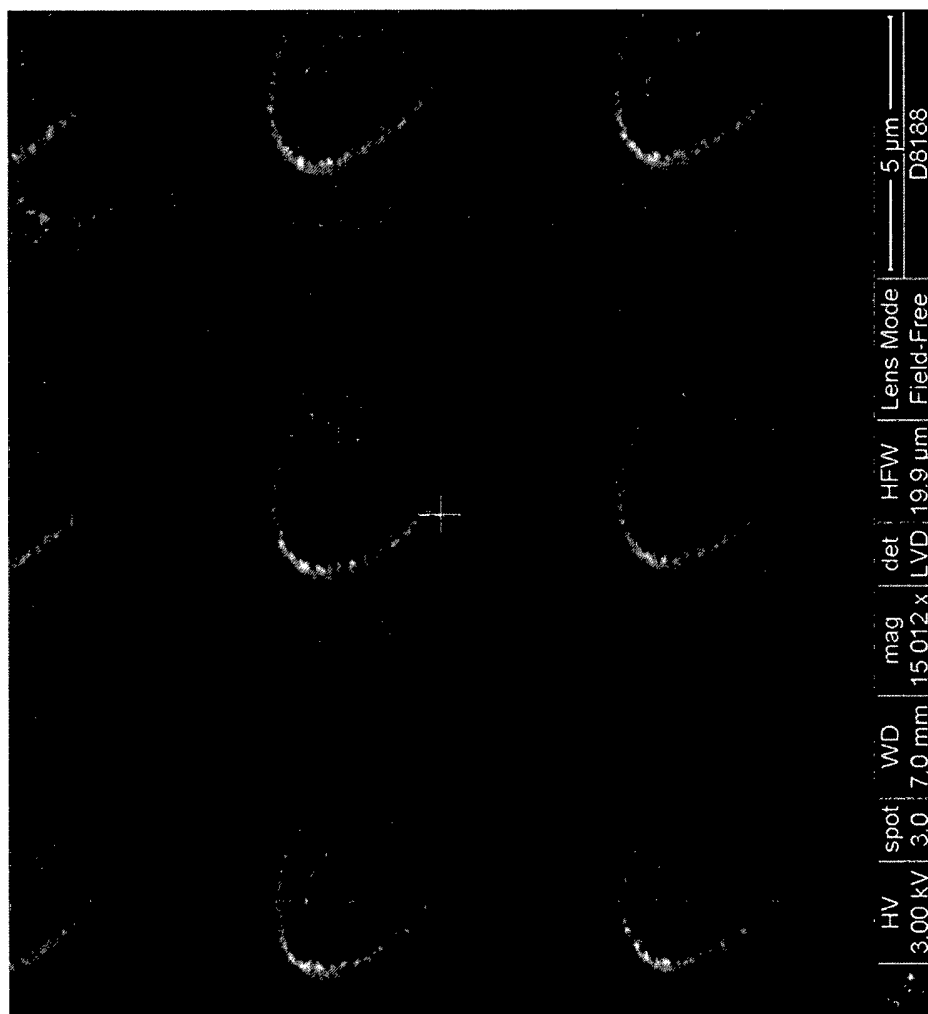


Fig. 10



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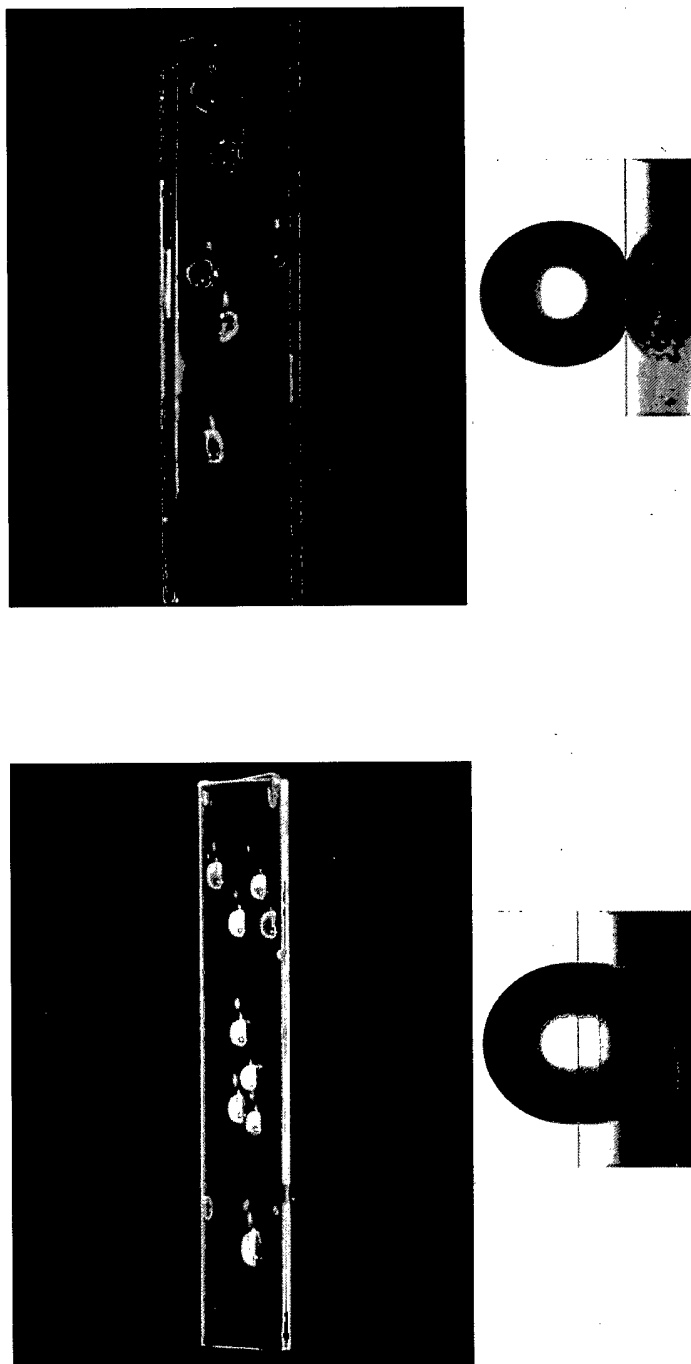


Fig. 11

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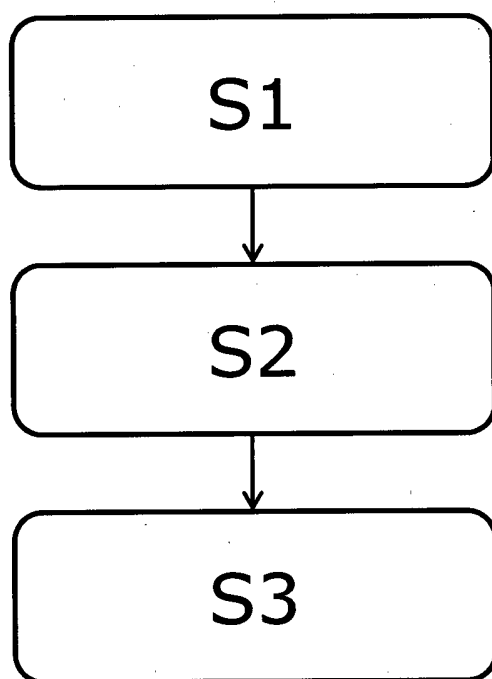


Fig. 12

# INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2013/050060

## A. CLASSIFICATION OF SUBJECT MATTER

INV. G03F7/00 B29C33/42 B29C45/26  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G03F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, IBM-TDB, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/115554 A1 (BREITUNG ERIC M [US] ET AL) 24 May 2007 (2007-05-24)	16
Y	paragraph [0020] - paragraph [0025]; figures 4,5 paragraph [0032]	1-15
	-----	
X	US 2011/287203 A1 (VICTOR JARED J [CA] ET AL) 24 November 2011 (2011-11-24)	16
Y	paragraph [0082] - paragraph [0087]; figure 1	1-15
	-----	
X	WO 02/22304 A1 (BAERLOCHER GMBH [DE]; HAUKE JUERGEN [DE]; REITH WALTER [DE]; KUENZINGER) 21 March 2002 (2002-03-21)	16
Y	page 3, line 12 - line 25 page 6, line 1 - line 8; claim 5	1-15
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	-/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

24 July 2013

Date of mailing of the international search report

01/08/2013

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# INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2013/050060

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>US 5 674 592 A (CLARK JOHN C [US] ET AL)</p> <p>7 October 1997 (1997-10-07)</p> <p>abstract; figures 2,4</p> <p>-----</p>	1-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/DK2013/050060

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007115554 A1	24-05-2007	TW 200823485 A US 2007115554 A1	01-06-2008 24-05-2007
US 2011287203 A1	24-11-2011	CA 2800381 A1 EP 2576171 A1 US 2011287203 A1 WO 2011147757 A1	01-12-2011 10-04-2013 24-11-2011 01-12-2011
WO 0222304 A1	21-03-2002	NONE	
US 5674592 A	07-10-1997	AU 5373996 A CA 2216378 A1 CN 1183739 A DE 69604915 D1 DE 69604915 T2 EP 0825901 A1 JP 3723218 B2 JP H11504281 A US 5674592 A WO 9634697 A1	21-11-1996 07-11-1996 03-06-1998 02-12-1999 18-05-2000 04-03-1998 07-12-2005 20-04-1999 07-10-1997 07-11-1996